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Spin fluctuation and single-ion effects in dilute UPt_3

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Single-ion effects are responsible for about 50% of the high γ ($\equiv C/T$ for $T\rightarrow 0$) in UPt_3. Diluting uranium in UPt_3 also shows that, contrary to usual expectations, γ and the low-temperature magnetic susceptibility χ do not seem to be strongly correlated. It is remarkable that the spin-fluctuation term ($T^3 \ln T$) in the low-temperature specific heat still appears, even down to a concentration of only 4% uranium. Comparisons to the doped heavy-fermion system $U_{1-x}M_xBe_{13}$ (with large x) are made.

I. INTRODUCTION

The intermetallic compound UPt_3 is still a focus of interest because of its unusual low-temperature properties. In single-crystal samples the magnetic parameters are strongly anisotropic: for field directions along the a and b axes a maximum in the magnetic susceptibility is observed[1] at about 16 K, with no such structure observed for fields parallel to the c axis. This maximum is also seen in polycrystalline samples. Although these data could be indicative (and were so interpreted[2] in the earliest measurements) of an arrangement of magnetic moments in a complex low-temperature magnetic structure, no sign of magnetic order near 16 K is found in the specific heat[1] or in the neutron scattering.[3] A pronounced $T^3\ln T$ term is observed in the specific-heat measurements, together with an unusually large value for the coefficient of the electronic term $\gamma=450$ mJ/mole K^2 ($\gamma\equiv C/T$ as $T\rightarrow 0$).[4] Because of the $T^3\ln T$ term, one usually interprets UPt_3 as a system with spin fluctuations.

Recent measurements[5] on $U_{1-x}M_xBe_{13}$ in the dilute limit show that about 60% of the low-temperature value of γ in UBe_{13} is due to single-ion effects. Similar measurements have been made on some Ce systems (i.e., $Ce_{1-x}La_xPb_3$, $Ce_{1-x}La_xCu_6$, and $Ce_{1-x}M_xCu_2Si_2$),[6,7] with, however, results in contrast to those for $U_{1-x}M_xBe_{13}$. For the compound $CePb_3$ both specific heat and magnetic susceptibility are independent of Ce concentration, while the low-temperature limit of the specific heat of $CeCu_6$ *increases* by about 40% with 90% Ce substituted by La. In $Ce_{1-x}M_xCu_2Si_2$, the results[7] are found to depend on M, allowing no general conclusions. These results lead to the obvious question: is the experimental result for UBe_{13} representative of uranium heavy-fermion systems?

In the previous work on UBe_{13} (Ref. 5) it was already pointed out that the problems in preparing dilute UPt_3 in some host lattices are (1) small amounts of doping materials in pure UPt_3 drive the samples into magnetism,[8] and (2) except for $PaPt_3$, no known MPt_3 compound exists with the same structure as UPt_3. Thus, in the present work we report studies of dilute UPt_3 by using $A_xB_yPt_3$ and doping U on either site A or B. These results are compared to the existing $U_{1-x}M_xBe_{13}$ results.[5] One advantage in using two metals instead of one is that, within some range, one can control the lattice parameters by changing x and y accordingly.

After several attempts to "create" the UPt_3 *DO*19 structure, four combinations have been found to be the most interesting: $Zr_xTa_yPt_3$, $Hf_xNb_yPt_3$, $Ta_xHf_yPt_3$, and $Nb_xZr_yPt_3$. The number of different elements in one unit cell makes it somewhat difficult to analyze the x-ray pattern precisely. The best results were obtained for the $Nb_xZr_yPt_3$ compound. Thus, in the following we will concentrate on the effects of doping U in this system. The results for the four pure $A_xB_yPt_3$ systems, as a function of the ratio of x and y, will be published elsewhere. It is interesting to note the fact[9] that $Nb_{0.65}Zr_{0.35}Pt_3$ orders in the UPt_3 *DO*19 structure has been known since 1966.

II. EXPERIMENTAL

Samples were prepared by arc melting together U (99.9%), M (typically 99.99%), and Pt (99.99%) in a purified Ar atmosphere. After remelting the samples at least twice they were checked for weight loss which was always smaller than 0.5%. All samples were characterized by x-ray diffraction. The correctness of the observed intensity ratios of the high-intensity peaks was checked by calculating the intensities of $Nb_xZr_yPt_3$ in the UPt_3 structure. As mentioned above, from the four possible $A_xB_yPt_3$'s, we found the best agreement between the measured and the calculated pattern to be $Nb_{0.65}Zr_{0.35}Pt_3$. However, after a certain amount of doping this system with U, some additional shoulders on some of the x-ray lines began to appear. Most of these peaks were found in $ZrPt_3$ as well, which is a Cu_3Au structure. The solubility of U in the observed compound was measured by the occurrence of these additional lines, as well as by measuring the lattice expansion of $Nb_{0.65}Zr_{0.35}Pt_3$ upon addition of U. We found that it is possible to dope up to 14% of U without getting any additional lines, and with no saturation in the monotonic increase in lattice parameters with increasing U content.

For all the x-ray patterns, we calculated an effective average atomic radius from the measured lattice constants, based on the *ad hoc* assumptions that (1) the atomic radius for U in UPt_3 is 1.542 Å, i.e., the one from Ref. 10, and (2) that the relative change for the atomic radius is equal to the relative change in the lattice parameters. (For example, in $Nb_{0.51}U_{0.14}Zr_{0.35}Pt_3$ for $a = 5.764$ Å and $c = 4.899$ Å, vs 5.846 Å and 4.969 Å for pure UPt_3, gives an effective U radius for this pseudobinary MPt_3 of 1.52 Å.) Figure 1 shows a plot of this effective atomic radius for all our samples. Attempts to make samples which are outside the borders of these plotted points failed, because we were unable to keep the pure *DO*19 structure. The calculated average atomic radius for uranium in $Nb_{0.65-x}U_xZr_{0.35}Pt_3$ increases from about 1.51 Å for $x = 0$ to 1.523 Å for $x = 0.14$. From this behavior (Fig. 1) we can estimate that at $x = 0.35$ we would reach the atomic radius for U in UPt_3, if $Nb_{0.3}U_{0.35}Zr_{0.35}Pt_3$ existed in the *DO*19 structure. The atomic radius for $x = 0.14$ is almost exactly in the middle between the value for $x = 0$ and the Zachariasen value of 1.542 Å. In any case, it is clear that U in $(NbZr)Pt_3$ is in a smaller host lattice that in UPt_3. Since hybridization between the U *f* electrons and the *d* electrons of Pt is known to be important, this closer spacing will again be discussed with our results below.

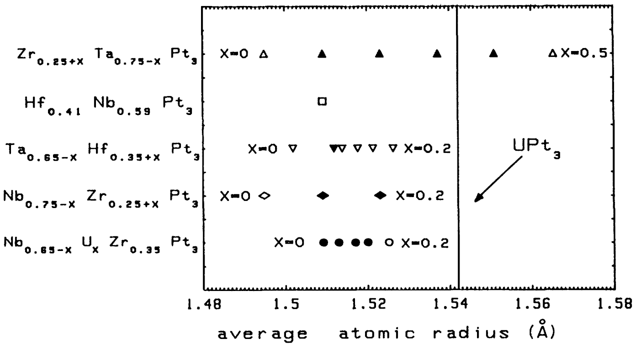

FIG. 1. Expected average atomic radius for U in several host materials, calculated from the relative change of the lattice parameters. The vertical line indicates the atomic radius for U from Ref. 10. The open symbols show samples which are not single phase. The three unlabeled points for $Nb_{0.65-x}U_xZr_{0.35}Pt_3$ have, from left to right respectively, $x = 0.05$, 0.1, and 0.14. For clarity, the points for $x = 0.01$, 0.02, 0.03, 0.04, 0.06, 0.07, and 0.12 are not shown. In addition to the undoped points shown, U was doped into $Zr_{0.25}U_{0.2}Ta_{0.55}Pt_3$(2-phased), $Zr_{0.35}U_{0.1}Ta_{0.55}Pt_3$(2-phased), $Zr_{0.45}U_{0.2}Ta_{0.35}Pt_3$(2-phased), $Zr_{0.35}U_{0.1}Ta_{0.55}Pt_3$(single-phased), $Zr_{0.45}U_{0.1}Ta_{0.45}Pt_3$(single-phased), and $Ta_{0.55}U_{0.1}Hf_{0.35}Pt_3$(single-phased). The effective U atomic radii for the three single-phased samples were 1.517 Å, 1.531 Å, and 1.510 Å, respectively, i.e., significantly below the value (1.542 Å) for pure UPt_3.

Susceptibility (from 1.8 to 300 K in a field of 5 kG) and magnetization versus field up to 5.5 T (at 2 K) were measured on all samples using an automated SQUID magnetometer from Quantum Design. Specific-heat measurements down to 1.2 K in zero field were made with a small mass calorimeter using a time constant method technique.[11]

III. RESULTS

A. Susceptibility

The dc susceptibility at 1.8 K for all the samples of $Nb_{0.65-x}U_xZr_{0.35}Pt_3$ is shown in Fig. 2. The values of χ (1.8 K) are normalized per U mole according to the formula

$$[\chi^{\text{measured}} - \chi(Nb_{0.65}Zr_{0.35}Pt_3)]/x \ ,$$

i.e., the background for $Nb_{0.65}Zr_{0.35}Pt_3$ is subtracted and the result normalized by the amount of U in the sample. In Fig. 2 one can see that there is a sample (i.e., $x = 0.03$) which has a significantly higher susceptibility than the others. Although we cannot rule this sample out as definitely spurious, we believe, based on our experience[8] with magnetism and defects in more concentrated $U_{1-x}M_xPt_3$, that this high χ value is likely due to defects in the *DO*19 lattice which depend critically on the thermal history of each sample.[12]

Thus the χ values from our bulk measurements (Fig. 2) cluster between about 4.5 and 6.5 memu/U mole and are essentially independent of U concentration in our doping range of $x \leq 0.14$. These values are, on average, within 20% of the value (see Fig. 2) for pure UPt_3. This result,

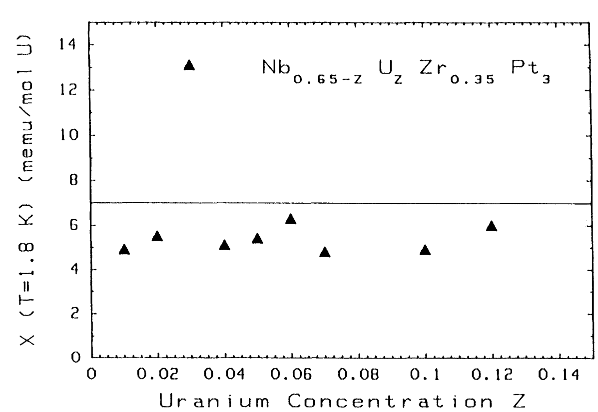

FIG. 2. Susceptibility of the compound $Nb_{0.65-x}U_xZr_{0.35}Pt_3$ vs U concentration *z*. All data are taken at 1.8 K and are normalized per U mole. The horizontal line in the picture shows the value for pure UPt_3 [Ref. 13] at 1.8 K.

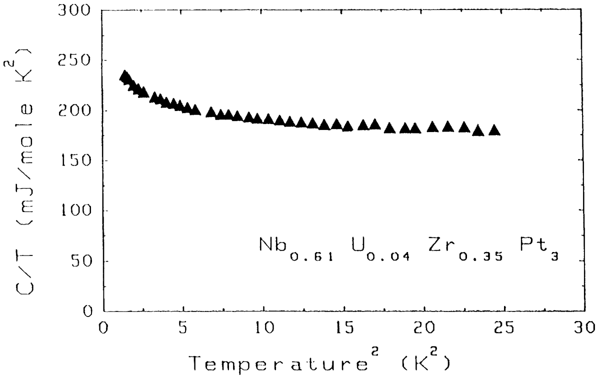

FIG. 3. Specific heat divided by temperature vs temperature squared of $Nb_{0.61}U_{0.04}Zr_{0.35}Pt_3$. The data for $Nb_{0.65}Zr_{0.35}Pt_3$ are subtracted and the result is divided by 0.04 to get the data normalized per U mole.

although somewhat uncertain due to the scattered $x=0.03$ data, is reminiscent of the doping results for $U_{1-x}M_xBe_{13}$, i.e., both dilute UPt_3 and dilute UBe_{13} appear to have χ essentially equal to that of the respective pure compound. This result is an apparent confirmation of the U concentration independence of χ previously found in $U_{1-x}M_xBe_{13}$.[5] Together with the specific-heat data discussed below this will give an idea of the mechanism that produces the high effective mass in UPt_3.

B. Specific heat

The main characteristic of heavy-fermion systems is the high value for $\gamma(\equiv C/T)$ as T approaches 0. For pure UPt_3, C/T increases about 50% as the temperature is lowered from 10 to 1 K. In this temperature range, C fits to the form $\gamma T+\beta T^3+\delta T^3 \ln T$ quite well.[4] The range below 1 K is hard to compare with our samples because UPt_3 becomes superconducting at about 500 mK.[4]

Figure 3 shows the result for a sample with 4% U (which in our notation is $x=0.04$). The specific heat of $Nb_{0.65}Zr_{0.35}Pt_3$ ($C/T=7.2$ mJ/ mole $K^2+0.24$ mJ/ mole $K^4 \times T^2$, i.e., quite small) is subtracted and the remaining C multiplied by a factor of 1/0.04 to get the correct values per U mole. We see that at 4% of U, γ is about 50% of the γ value per U mole for pure UPt_3.

Figure 4 shows the measurement for 10% U, normalized in the same way as the data for 4% doping. Within the error limits of our measurements, the values for $C/T(T\rightarrow 0)$ are the *same* for both samples. Other specific-heat measurements on $x=0.02$ and $x=0.14$ in $Nb_{0.65-x}U_xZr_{0.35}Pt_3$ (not shown) support this conclusion, i.e., between $x=0.02$ and $x=0.14$ γ per U mole is constant within $\pm 8\%$. Thus, within the error limits of our measurements we get a constant γ for dilute U in our $A_xB_yPt_3$ host $DO19$ lattice of about 50% of the value for pure UPt_3.

IV. DISCUSSION

Our results for the magnetic susceptibility χ and the coefficient γ in the low-temperature specific heat for the system $Nb_{0.65}Zr_{0.35}Pt_3$ doped with U are similar to the measurements[5] on $U_{1-x}M_xBe_{13}$. It is obvious that in the present work there are some problems in getting reproducible answers for the magnetic susceptibility χ. This is not only a problem for our series of samples, it is also seen to a lesser extent in pure UPt_3.[13] As discussed above, this sample dependence of χ is possibly due to some stress dependence of the magnetic correlations (spin fluctuations) in UPt_3. Thus, through some stacking faults we get a "new structure" which has two elementary cells of the $DO19$ structure above each other in its elementary cell (the hexagonal $DO24$ structure). This leads to a "local second phase" which is then undetectable by x-ray diffraction, due to the lack of long-range order. This simple explanation is consistent with our specific-heat measurements, since the sample ($x=0.02$, see Ref. 12) with high χ shows no change in the γ value. Thus, we believe that the intrinsic value of χ, ignoring the one scattered point, like our measured dilute-limit γ, is not a function of U concentration.

The observed γ per U mole in the present work, i.e., about 50% of that seen in pure UPt_3, coupled with the

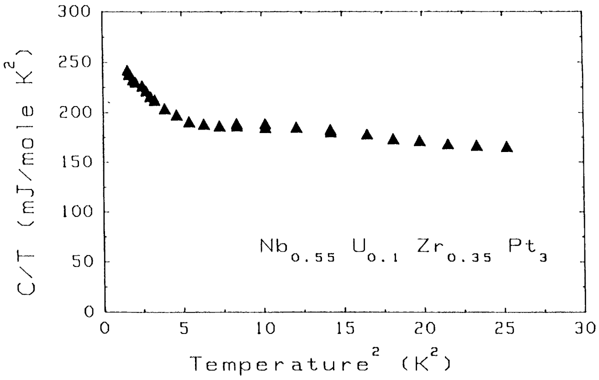

FIG. 4. Specific heat divided by temperature vs temperature squared of $Nb_{0.55}U_{0.1}Zr_{0.35}Pt_3$. The data are normalized in the same manner as in Fig. 3.

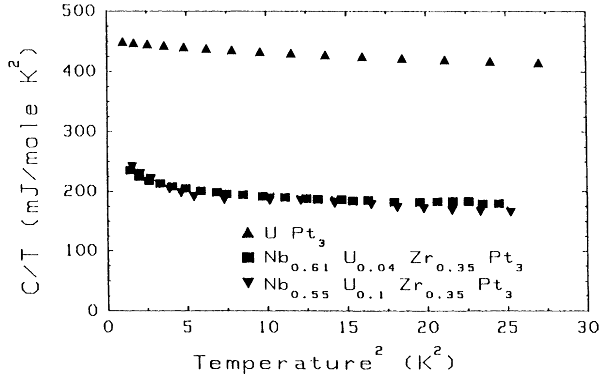

FIG. 5. Specific heat divided by temperature vs temperature squared of UPt_3 (data are from Ref. 13), $Nb_{0.61}U_{0.04}Zr_{0.35}Pt_3$, and $Nb_{0.55}U_{0.1}Zr_{0.35}Pt_3$. The data of the latter two are normalized in the same manner as in Fig. 3.

essential equality of χ with that of pure UPt$_3$, is the same result as observed in the only other U heavy-fermion system dilution study, i.e., the work[5] on $U_{1-x}M_xBe_{13}$. Thus, just as in $U_{1-x}M_xBe_{13}$, we may conclude that χ and the correlation which produced half of γ are *not* related, while the single-ion, dilute-limit half of γ could well be related in its mechanism to the large χ value observed at low temperatures. Additionally, and what was not expected, is that the $T^3\ln T$ spin-fluctuation temperature dependence of the specific heat in UPt$_3$ is *unchanged* in the dilute limit (see Figs. 3, 4, and 5).

It is important to stress that our measured γ for "dilute" UPt$_3$ is in $Nb_{0.65-x}U_xZr_{0.35}Pt_3$, which has significantly smaller lattice parameters ($\approx 1\%$) than pure UPt$_3$. A 50% decrease of γ in UPt$_3$ with 10 kbar pressure has been measured.[14] (It should be noted that based on the known Grüneisen parameter, the effective pressure needed to reduce the lattice parameter in UPt$_3$ to that observed in our $Nb_{0.65}Zr_{0.35}Pt_3$ samples is more than 20 times that used in the published specific-heat versus pressure experiments.) However, at least in the range of lattice parameters that our data presented here span in the dilute limit, γ per mole of U in $Nb_{0.65-x}U_xZr_{0.35}Pt_3$ is not lattice parameter dependent.

In conclusion, our results for "dilute UPt$_3$" are consistent with conclusions reached for $U_{1-x}M_xBe_{13}$, i.e., about one-half of the measured γ in the concentrated U heavy-fermion system is a single-ion effect; γ are χ are not strongly interconnected. Further, spin fluctuations still appear to be present in dilute UPt$_3$.

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